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14. ABSTRACT

The subject of this project is the synthesis and characterization of a new class of molecular components for nematic-based liquid crystal displays that show good solubility in the nematic host and high efficiency at low doping levels. The centerpiece of the design is the inorganic boron cluster CB11H12(-) which upon substitution with a positively charged group forms highly polar, UV transparent liquid crystal materials.

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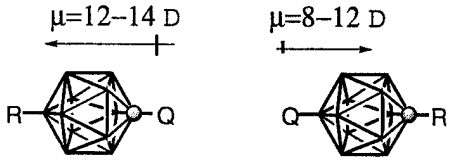
A New Class of Highly Polar Liquid Crystals
for Display Applications

I. Goals

- Development of new liquid crystalline components for nematic mixtures which will lower the operational voltage of devices, increase photostability, and permit construction of thin film cells.
- The key structural element for the design of this new class of liquid crystals is an inorganic 12-vertex monocarbaborate cluster, $CB_{11}H_{12}(-)$, whose negative charge is compensated with a positively charged substituent Q (Figure 1).



Type I *Type II*

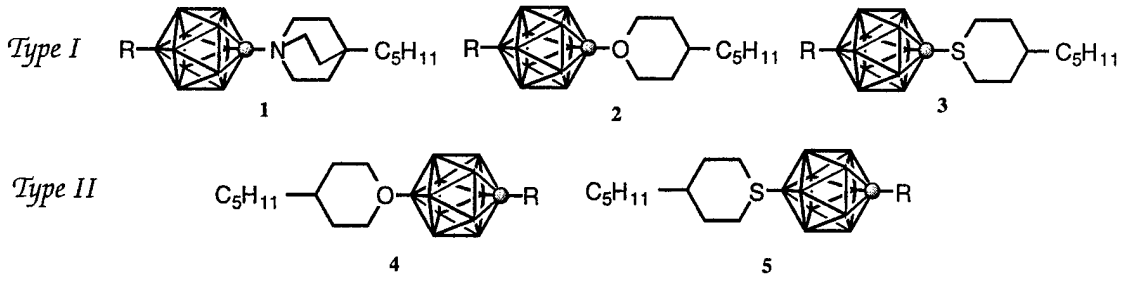
Figure 1. Two types of betaines derived from carbadodecaborate anion $CB_{11}H_{12}(-1)$. Each unsubstituted vertex corresponds to a BH fragment and the sphere represents a carbon atom. R is an alkyl group and Q is an onium substituent such as pyridinium, quinuclidinium, sulfonium and oxonium. The arrows indicate the direction and the relative magnitudes of dipole moments μ.

- Key features of the new materials:

  1. Large dipole moments of about 12-14 D rigidly oriented along the long molecular axes. (This property gives a lower operational voltage for the electrooptical device)
  2. UV transparency above 210 nm. (This increases photostability of the material.)
  3. Low birefringence and high refractive index. (This allows for thinner layers of the liquid crystal material.)

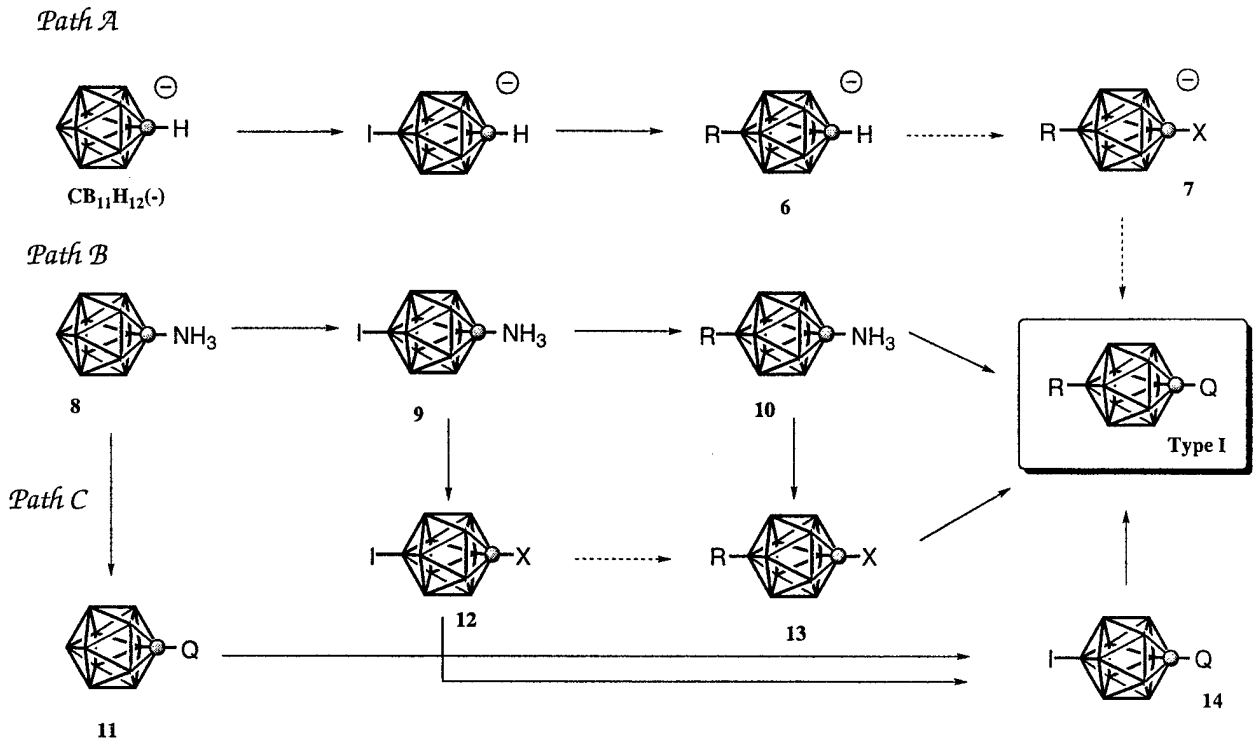
II Synthetic Strategy

- The onium group Q has been chosen as: quinuclidine (**1**), tetrahydropyran (**2**, **4**) and tetrahydrothiopyran (**3**, **5**), each substituted with pentyl groups. The alkyl group attached to the cage was initially chosen to be either pentyl (**a**) or decyl (**b**).



a, R=C_5H_{11}, **b**, R=$C_{10}H_{21}$,

- Our initial focus was on Type I liquid crystals and Scheme 1 shows synthetic pathways to this class of materials.



- Path A relies on C-functionalization of the 12-alkyl derivative **6** whose reliable synthesis was recently described in the literature (Gruner *et al, J. Am. Chem. Soc.*, **1999**, *121*, 3122).
- Path B starts from C-amino derivative **8** which is substituted in the 12 position with an alkyl group. The amino group serves as a synthetic handle to introduce the two other heteroatoms via diazotization either as X (OH_2 and SH_2) or onium groups Q, and is also converted into the C-quinuclidine derivative **1**.
- Path C is derived from the method, which we used previously to prepare the first quantities of the quinuclidine derivatives **1a** and **1b**.

III. Challenges

- 1,12 Difunctionalization of the $CB_{11}H_{12}$ cluster was virtually unknown and the first approaches were developed by us (Path C).
- Characterization of electro-optical performance of highly polar materials.

IV. Results

Synthesis

- The original synthesis of **1** along Path C was very inefficient.
- Significant difficulties were encountered with C-functionalization of 12-alkyl carbaborates. Reactions with electrophiles that typically give moderate to good yields for the parent cluster $CB_{11}H_{12}(-)$, were ineffective in the case of 12-alkyl derivatives **6** (Path A).
- We discovered that iodination of amine **8** gives good yields of the 12-iodo derivative **9**, which, in turn, undergoes particularly efficient Pd-catalyzed coupling reactions to yield 12-alkyl derivatives **10** (Path B).
- Following Path B, we have prepared significant quantities (>0.25 g) of the quinuclidine derivatives **1** and completed their characterization including single crystal X-ray analysis.
- The C-amino derivative **10** was successfully converted into the C-hydroxy derivative **13** ($X=OH_2$) by diazotization. The alkylation step turned out to be more difficult than we anticipated but we found solution to this problem.
- A reproducible and efficient synthesis of the **13** ($X=SH_2$) from the C-amino derivative **10** still poses a challenge despite the initial observation of the desired product.

Characterization

- The dipole moment for **11** (Q = quinuclidine) was measured to be 12 D (calculated 14 D)
- Solubility in a nematic host for **1** has been evaluated
- Electrooptical performance of **1** in two nematic hosts has been done
- Roentgenographic characterization of the LC phases for **1** is complete.

Computational analysis

All calculations have been performed using ab initio quantum-mechanical methods.

- Dipole moments have been calculated and compared with the experimental value.
- Conformational analysis for the **1** and **2** is almost complete.
- Evaluation of energy barriers to inversion at the O and S centers (in **2** and **3**, respectively) is begun. (This is an important factor governing the isomeric composition for the compounds).
- Account for different reactivity of 12-iodo derivatives towards Grignard reagents is complete.

V. Accomplishments

- A facile methodology for 1-12 difunctionalization of the $CB_{11}H_{12}$ clusters
- Practical synthesis of the quinuclidine derivatives **1**
- Identification of the LC phases by powder XRD for **1**
- Studies of electrooptical performance of the quinuclidine derivatives **1**

- Theoretical understanding molecular properties of the mesogens.

VI. Publications with acknowledgment of the grant support

1. Pakhomov, S.; Kaszynski, P.; Young, V. G. Jr. *Inorg. Chem.*, **2000**, *39*, 2243-2245.

2. Kaszynski, P. in *Anisotropic Organic Materials-Approaches to Polar Order,* R. Glaser and P. Kaszynski, Eds. ACS Symposium Series, Volume 798. American Chemical Society, Washington, D.C. 2001, pp 68-82.

3. Pakhomov, S.; Douglass, A. G.; Balisnki, A.; Kaszynski, P., *J. Am. Chem. Soc.*, in preparation.